

## PROCESS FOR PRODUCING MAGNETITE PARTICLES

### BACKGROUND OF THE INVENTION

The invention relates to a process for producing magnetite particles.

Particulate magnetites produced from aqueous solutions by a precipitation process have been known for a long time. The production of magnetite by precipitation of iron(II) sulfate using an alkaline component and subsequent oxidation by air has already been described in US-A 802 928. The production of magnetites by the precipitation process is likewise described in numerous subsequent publications.

The production of magnetites by the precipitation process with the addition of silicon is described in JP-A 51 044 298. Pure precipitated magnetites without added foreign elements can be produced batchwise according to DE-A 3 209 469 or continuously according to DE-A 2 618 058. Normally, the iron(II) salt used is  $\text{FeSO}_4$ .

It is possible, however, to use any soluble iron(II) salt for the production of a magnetite by the precipitation process. The use of  $\text{FeCl}_2$ , as described in DE-A 3 004 718, is particularly suitable here. The use of  $\text{FeSO}_4$  or of  $\text{FeCl}_2$  has the advantage that both substances can be obtained very economically in large quantities as waste products of the iron-working industry. Suitable precipitating agents, besides the most frequently used sodium hydroxide, are  $\text{CaO}$  or  $\text{CaCO}_3$  (DE-A 3 004 718), ammonia (DE-A 2 460 493) or  $\text{Na}_2\text{CO}_3$ ,  $\text{MgCO}_3$  or  $\text{MgO}$  (EP-A 0 187 331). Air is generally used as the oxidizing agent. However, oxidation processes using nitrates (DD-A 216 040 and DD-A 284 478) are also described.

The magnetites have been used primarily for producing all kinds of pigments. The particular advantage of magnetites over organic pigments and carbon black is their far better resistance to weathering, so that pigments containing magnetite can also be used outdoors. Precipitated magnetites are also usually employed for coloring concrete moldings such as concrete paving stones or concrete roofing tiles.

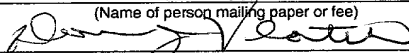
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Magnetites have also been used for a long time in electro-  
photography for the production of toners. Magnetites which have been  
obtained by the precipitation process are preferably employed for  
producing toners for photocopiers using one-component toners. The  
5 magnetic toners used for this purpose must have several properties. With  
the progressive development and improvement of photocopiers and  
printers, ever greater demands are placed on the magnetic toners and  
consequently on the magnetite used in them. The most recent generation  
of printers achieves a resolution of more than 400 dpi (dots per inch), for  
10 which it was necessary to develop finely divided toners having a very  
narrow particle-size distribution. The result of this was that the magnetites  
used for this purpose must likewise possess a very narrow particle-size  
distribution. A specific particle size is also necessary in order to ensure a  
homogeneous distribution of the magnetite particles in the final toner. The  
15 magnetites must themselves have an electrical resistance high enough to  
stabilize the latent image during electrostatic transfer. Furthermore,  
coercivity, saturation magnetization and, above all, the remanent  
magnetization must all be in the correct relationship to the field strengths  
prevailing in the machine.

20 It is an object of the present invention to provide a technically  
particularly simple and therefore also economic process for producing  
magnetites having a coercivity of 80 to 130 Oe (= 6.366 kA/m to 10.345  
kA/m) and an octahedral particle shape for the production of magnetic  
toners. This object can be achieved by the process according to the  
25 invention.

#### SUMMARY OF THE INVENTION

The invention relates to a process for producing a magnetite having  
a coercivity of 6.366 kA/m to 10.345 kA/m (= 80 to 130 Oe) and an  
octahedral particle shape by

- 30 a) placing an alkaline component in the form of an aqueous  
solution under a protective gas,  
b) heating the alkaline component to a temperature of 50°C to  
100°C,

- 5 c) adding an iron(II) component in the form of an aqueous solution whereby the molar ratio of iron(II) component to one equivalent of alkaline component is 0.38 to 0.45, while maintaining the temperature at 50°C to 100°C,
- d) treating the suspension obtained in c) with an oxidizing agent, whereby the rate of oxidation is 20 to 50 mol.% Fe(II)/h until the iron compound has an Fe(III) content of more than 65 mol.%,
- 10 e) after the oxidation in d), again adding an Fe(II) component in the form of an aqueous solution to the suspension obtained in d) whereby the molar ratio of Fe(II) in c) to one equivalent of total alkaline component used is 0.47 to 0.49,
- f) treating the suspension obtained in e) with an oxidizing agent, whereby the rate of oxidation is 20 to 50 mol.% Fe(II)/h until the iron compound has an Fe(III) content of more than 65 mol.%,
- 15 g) filtering the suspension, and washing, drying and grounding the residue.

#### DETAILED DESCRIPTION OF THE INVENTION

20 Surprisingly, it has been found that by increasing the ratio of Fe(II) to alkaline component to 0.38 to 0.44, at temperatures of 50°C to 100°C, preferably at 70°C to 90°C, and by rapid oxidation (up to 50 mol.% Fe(II)), a magnetite which is usable in standard toners is obtained. Owing to the high rate of oxidation, the process is particularly economical because the

25 plants can be utilized particularly efficiently.

The magnetites thus obtained can be used not only in magnetic toners, but also for coloring paper, plastic, paints, fibres and concrete, and in dyes.

30 Magnetites having a coercivity of 80 to 130 Oe (= 6.366 kA/m to 10.345 kA/m) and an octahedral particle shape are obtainable by the following process according to the invention, wherein

- a) an alkaline component in the form of an aqueous solution is placed under a protective gas,

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- 5 b) the alkaline component is heated to a temperature of 50°C to 100°C, preferably to 70°C to 90°C,
- c) an iron(II) component in the form of an aqueous solution is added in a quantity such that the molar ratio of iron(II) component to one equivalent of alkaline component is 0.38 to 0.45, the temperature being maintained at 50°C to 100°C, preferably 70°C to 90°C,
- 10 d) the suspension obtained in c) is treated with an oxidizing agent, with a rate of oxidation of 20 to 50 mol.% Fe(II)/h being established, until the iron compound has an Fe(III) content of more than 65 mol.%,
- e) after the oxidation in d), an Fe(II) component in the form of an aqueous solution is again added to the suspension obtained in d) in a quantity such that the molar ratio of Fe(II) used in c) to one equivalent of total alkaline component used is 0.47 to 0.49,
- 15 f) the suspension obtained in e) is again treated with an oxidizing agent, with a rate of oxidation of 20 to 50 mol.% Fe(II)/h being established, until the iron compound has an Fe(III) content of more than 65 mol.%, and then
- 20 g) filtered and the residue is washed, dried and ground.

The alkaline component preferably contains an alkali metal hydroxide, an alkaline-earth metal hydroxide, an alkaline-earth metal oxide, an alkali metal carbonate,  $\text{MgCO}_3$  or ammonia

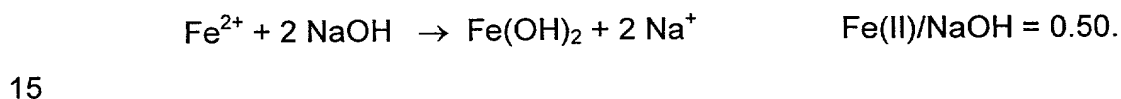
- 25 The iron (II) component preferably contains a water-soluble Fe(II) salt, more preferably an iron sulfate or iron dichloride. It is also possible, however, to use other water-soluble Fe(II) compounds, in particular if they are available at comparable prices.

- 30 The oxidizing agent preferably contains atmospheric oxygen, pure oxygen,  $\text{H}_2\text{O}_2$ , chlorine, alkali metal chlorates (for example,  $\text{NaOCl}$ ,  $\text{NaClO}_3$ ,  $\text{NaClO}_4$ ) or nitrates. Atmospheric oxygen, pure oxygen,  $\text{H}_2\text{O}_2$  or sodium nitrate are more preferred.

A particularly preferred embodiment of the process according to the invention is described in more detail below.

Sodium hydroxide solution containing 300 g NaOH per liter of water is placed in a batch-operated stirred-tank reactor, with stirring under a flow  
5 of protective gas.

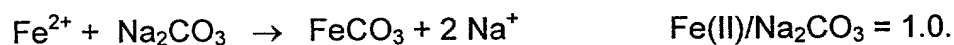
The solution is then heated to a temperature of between 50°C and 100°C, preferably between 70°C and 90°C. When this temperature has been attained, metering of the Fe(II) component is commenced. The Fe(II) component is calculated from the desired NaOH/Fe(II) ratio. If, for  
10 example, the aim is to achieve an NaOH/Fe(II) ratio of 0.55 and 100 mol NaOH has been introduced, then  $100 \times 0.55 = 55$  mol Fe(II) component must be added. The calculation of the alkali metal hydroxide/Fe(II) ratio is based on the equation



If an alkaline component is used which reacts in a different stoichiometric ratio with the Fe(II) component to form Fe(OH)<sub>2</sub> or FeCO<sub>3</sub>, the ratio must be correspondingly altered. This is the case, for example, where carbonates or alkaline-earth metal hydroxides or alkaline-earth  
20 metal oxides are used, so that in these cases the equation is as follows:



or



25 The Fe(II) component is metered preferably at such a rate such that no fall in temperature occurs. When the addition of the calculated quantity of the Fe(II) component is complete, the reaction mixture is optionally heated once more to 50°C to 100°C. In many cases the temperature in b) and the temperature in c) are identical, so that a further heating step is not  
30 required in c). When this temperature has been attained, the aeration with protective gas is concluded and the addition of the oxidizing agent is commenced. In the case of an aeration using air, air is introduced via an aeration device below the stirrer. The quantity of air supplied per hour is

between 5 and 15 l/h per mol Fe(II). Where NaNO<sub>3</sub> is used, the oxidizing agent is pumped in as an aqueous solution over a period of 5 to 30 minutes. The quantity required can be calculated from:

$$\text{NaNO}_3 [\text{mol}] = \text{Fe(II)} [\text{mol}] * 0.67 * 1/8.$$

5 For example, 100 mol Fe(II) would therefore require 8.375 mol NaNO<sub>3</sub>. The quantities of the other oxidizing agents are calculated from the redox equivalents of the respective oxidizing agents. Here it should be borne in mind that at most only 66.6% of the Fe(II) has to be oxidized in order to produce magnetite.

10 The oxidation is concluded preferably when an Fe(III) content of more than 65 mol.% has been attained. This can be ascertained by redox titration.

Following this oxidation, an aqueous solution of an Fe(II) component is added until a ratio of Fe(II)/alkaline component of 0.47 to  
15 0.49 is established. This further addition of Fe(II) serves to completely utilize the alkaline component used. If this step were not carried out, a considerable proportion of the alkaline component would enter the waste water, where it would have to be neutralized at some expense. Subsequently, oxidation is resumed at a rate of up to 50 mol.% Fe(II)/h,  
20 until an Fe(III) content of more than 65 mol.% is attained.

On conclusion of the second oxidation, the product is filtered, washed and dried. Prior to being dried, the product can be aftertreated in order to improve the thermostability and dispersibility. A polysiloxane or organic Ti ester can be preferably used for this.

25 The preferred conditions are as follows:

- alkaline component: NaOH
- Fe component: FeSO<sub>4</sub>
- reaction temperature: 80°C to 90°C
- FeSO<sub>4</sub>/NaOH: 0.43 to 0.41
- 30 - rate of oxidation: 35 to 50 mol.% Fe(II)/h
- FeSO<sub>4</sub>/NaOH after the first oxidation: 0.48

The magnetites produced by the process according to the invention or the magnetites according to the invention can be used with particular

advantage for the production of toners, printing inks and dye pastes for ink-jet printers.

The properties of the magnetites were measured by the following methods:

- 5           1.       The color values were examined by preparing a paint:

3.2 g magnetite was ground in a microdismembrator (30") using an agate sphere of 10 mm in diameter. Then 2.0 g of the binder Alkydal® F48 (Bayer AG, Leverkusen, DE), 0.1 g of the ground magnetite to be examined and 1.0 g TiO<sub>2</sub> (Bayertitan® R-FK2; Bayer AG, Leverkusen, 10 DE) were ground on a plate color rubbing machine (product of Engelsmann) having a diameter of 250 mm (also referred to as a muller).

The color values L\* (brightness), a\* (red) and b\* (blue) were determined in accordance with DIN 55986, using Dataflash 2000 (d/8°), instrument A and the evaluation programme CIELAB 2 dated 19.10.1989.

- 15       The entire procedure of color measurement is described in detail in EP-A 0 911 370.

2.       The magnetic values (coercivity, specific saturation magnetization, specific remanent magnetization) were measured by a magnetometer (product of Bayer) at 5000 Oe field strength (corresponding 20 to 397.9 kA.m<sup>-1</sup>).

3.       The BET surface area was measured in accordance with DIN 66 131. Gas mixture: 90% He, 10% N<sub>2</sub>; measuring temperature: 77.4 K; heating at 140°C, 60 minutes.

4.       Elemental analysis for Si and Mn:

25       Si was determined by spectral analysis, using ICP-OES. Mn was determined by atomic absorption spectroscopy.

5.       Elemental analysis for Fe (total), Fe(II) and Fe(III):

Determinations in accordance with DIN 55 913. The Fe content was determined by titration with KMnO<sub>4</sub> using a memotitrator (Mettler DL-70).

30       The Fe(III) was determined similarly, using TiCl<sub>3</sub>. The total iron content was calculated from the two individual values and the weighed portion. The concentrations of the two standard solutions were determined daily.

## 6. Particle shape and particle size:

Assessment of the particle size and particle shape from a transmission electron microscope (TEM) micrograph at 30,000 times magnification.

## 5 7. Elemental analysis for S:

Sulfur was determined by ICP-OES.

8. The water-soluble constituents were determined in accordance with ISO-EN 787 Part 3.

9. The pH value of the magnetite powder was determined in  
10 accordance with ISO-EN 787 Part 9.

The invention is illustrated in more detail by the following Examples.

EXAMPLESExample 1

15 7876 g sodium hydroxide solution containing 300 g/l NaOH, corresponding to 46.67 mol NaOH, was placed in a stirred-tank reactor having a useful volume of 30 liters. The supply of nitrogen for aeration and the stirrer were set in operation and the sodium hydroxide solution was then heated to 80°C. Then 13.430 liters of iron(II) sulfate solution  
20 containing 237.54 g/l Fe(II), corresponding to 21 mol Fe(II), was pumped in over a period of 45 minutes. The FeSO<sub>4</sub>/NaOH ratio was 0.45. The nitrogen supply was then turned off and the reaction mixture was aerated by means of 200 l/h air through an aeration ring installed below the stirrer. Aeration was discontinued when an Fe(III) content of 66 mol.% had been  
25 attained; subsequently aeration was resumed, using nitrogen. 1100 ml of FeSO<sub>4</sub> solution containing 237.54 g FeSO<sub>4</sub> per liter, corresponding to 1.72 mol FeSO<sub>4</sub>, was then pumped in over period of 6 minutes. At this point, the FeSO<sub>4</sub>/NaOH ratio was 0.487. The reaction mixture was then oxidised by 200 l/h air until the Fe(III) content was 66.8 mol.%.

30 On conclusion of oxidation, the suspension was filtered, washed thoroughly using deionized water and dried in air at 80°C. The powder obtained was ground in an impact mill.

The rate of oxidation was 28 mol.% Fe-II/h.



The magnetite obtained had the following properties:

	brightness L*	: 60.1 CIELAB
	a*	: -0.3 CIELAB
	b*	: -6.8 CIELAB
5	coercivity	: 105 Oe = 8.355 kA/m
	specific saturation magnetism	: 114.7 nT/m <sup>3</sup>
	specific remanence	: 24.1 nTm <sup>3</sup> /g
	particle size	: 0.3 µm
	S content	: 0.02 wt.%, determined as SO <sub>3</sub>
10	Mn content	: 0.21 wt.%
	water-soluble constituents	: 0.13 wt.%
	DIN pH value	: 8.2
	temperature stability	: 140°C
	Fe(II) content	: 29.1 mol.%
15	particle shape	: octahedral

### Example 2

- 6800 kg NaOH, in the form of a solution containing 300 g/l NaOH, corresponding to 170 kmol NaOH, was placed in a stirred-tank reactor
- 20 having a useful volume of 100 m<sup>3</sup>. The supply of nitrogen for aeration and the stirrer were set in operation and the sodium hydroxide solution was then heated to 90°C. Then 39.3 m<sup>3</sup> of iron(II) sulfate solution containing 269.57 g/l Fe(II), corresponding to 69.74 kmol Fe(II), was pumped in over a period of 22 minutes. The FeSO<sub>4</sub>/NaOH ratio was 0.41. The nitrogen
- 25 supply was then turned off and the reaction mixture was aerated by means of 475 m<sup>3</sup>/h air through an aeration ring installed below the stirrer. Aeration was discontinued when an Fe(III) content of 67 mol.% had been attained; subsequently aeration was resumed, using nitrogen. Then 5.9 m<sup>3</sup> of iron(II) sulfate solution containing 269.57 g/l FeSO<sub>4</sub> per liter,
- 30 corresponding to 10.47 kmol FeSO<sub>4</sub>, was pumped in. At this point, the FeSO<sub>4</sub>/NaOH ratio was 0.472. The reaction mixture was then oxidised by 475 m<sup>3</sup>/h air until the Fe(III) content was 66.8 mol.%.

The rate of oxidation was 22 mol.%/h

On conclusion of this reaction, the suspension was filtered, washed thoroughly using deionized water and spray dried in waste gas at 110°C.

The powder obtained was ground in an impact mill.

5 The magnetite obtained had the following properties:

brightness L\* : 60.9

a\* : -0.3

b\* : -6.6

BET surface area : 4.2 m<sup>2</sup>/g

10 coercivity : 110 Oe = 8.753 kA/m

specific saturation magnetizm : 109.3 nT/m<sup>3</sup>

specific remanence : 20.9 nTm<sup>3</sup>/g

particle size : 0.4 μm

S content : 0.09 wt.% SO<sub>3</sub>

15 Mn content : 0.24 wt.%

water-soluble constituents : 0.19 wt.%

DIN pH value : 8.6

Fe(II) content : 29.0 mol.%

particle shape : octahedral

20 Although the invention has been described in detail in the foregoing for the purpose of illustration, it is to be understood that such detail is solely for that purpose and that variations can be made therein by those skilled in the art without departing from the spirit and scope of the invention except as it may be limited by the claims.